OXIDATION OF O-NITROTOLUENE

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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OXIDATION OF O-NITROTOLUENE TO O-NITROBENZOIC ACID

A THESIS

PRESENTED BY
WILLIAM S. EAGLE, JR. AND HENRY F. KLEMM
TO THE
PRESIDENT AND FACULTY
OF
ARMOUR INSTITUTE OF TECHNOLOGY
FOR THE DEGREE OF
BACHELOR OF SCIENCE
IN
CHEMICAL ENGINEERING

MAY 27, 1920

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OXIDATION OF O-NITRO TOLUOL TO O-NITRO BENZOIC ACID

INTRODUCTION

The object of this research is to determine whether anthranilic acid (o-amino benzoic acid) could be made commercially from a comparatively cheap material such as the corresponding nitro-toluol, and to determine the conditions under which the necessary steps should be carried out in order to produce a product capable of being manufactured in competition with anthranilic acid as now made. Anthranilic acid is not ordinarily obtainable in the open marked inasmuch as most manufacturers use all they make for the synthesis of indigo. It is, therefore, difficult to get a reliable figure on the present market price, but it seems that a fair value at the present time is $3.50 per pound in commercial quantities.

At present the method of manufacture is, briefly, this:[1] naphthalene is oxidized to phthalic anhydride by heating it with sulfuric acid in the presence of mercuric sulfate. Phthalic anhydride

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1. Perkin and Kipping "Organic Chemistry", P.664

is converted to phthalimide by heating it with ammonia under pressure, and the phthalimide is converted to anthranilic acid by heating it with an alkali hypochlorite.

There are many other methods by which anthranilic acid may be obtained but a review of the literature seems to show that most of them, either because of the difficulties involved in carrying them out, or because of the cost of materials or reagents involved, are of purely theoretical rather than practical interest. It may, however, be of value to cite a few of these.

It is evident, of course, that the general method of oxidation may be applied by suitable modification of the conditions, to o-nitro-toluol, o-nitro benzaldehyde, o-nitro benzyl halide,[1] alcohol, or aldehyde with subsequent reduction of the nitro group and, in general, it may be said that the partially oxidized compounds listed above are more readily oxidized to the acid than is the toluol. In every case, however, the ortho isomer is the most difficult of the three possible

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[1] Berichte 17,386 (1884)

isomeric forms to oxidize, as would be expected from the usual inhibitory action of the negative group in the ortho position. In addition to the above listed possibilities there is also the ortho toluidene which, when acetylated to protect the amino group, may be oxidized with potassium permanganate and saponified to a salt of anthranilic acid. Of the above possibilities the toluol and toluidene are the only two materials commercially available at a reasonable price, and of the two the toluol is slightly the cheaper. The protection of the amino group during oxidation is hardly a commercial possibility and thus the toluol appears to be the logical raw material to start with.

Assuming then that a fairly pure o-nitro toluol such as is available in large quantities is used, several interesting possibilities are at once apparent. One such suggests itself immediately inasmuch as both anthranilic acid and o-nitro toluol have the same empirical formula $C_7H_7NO_2$ and at once give rise to the possibility of an intramolecular rearrangement to produce the desired result. A simple calculation of the heats of formation of anthranilic acid and of o-nitro toluene will show that such a rearrangement is at least

theoretically possible, the former having a considerably lower heat of formation than the latter. Two methods for bringing about this change have been described.

[1] Liquid bromine is allowed to drop slowly into o-nitro toluene heated under a reflux condenser to 170°. The action is strongly exothermic and, once started, needs no external application of heat, the temperature being controlled by the speed of addition of the bromine. When the theoretical amount of Br_2 in equi-molecular proportions has been added, allow the solution to cool. Warm it slightly and treat with a solution of sodium carbonate. Acidify with acetic acid and filter off the 3-5 dibrom-ortho-amino-2 benzoic acid as a cheesy, yellowish-white precipitate. Heat the acid with a solution of barium carbonate, filter off any tar, acidify, and again filter off the dibrom anthranilic acid. Recrystallize from alcohol.

A second interesting rearrangement of o-nitro-toluol to anthranilic acid may be brought about in the presence of alkali hydroxides.[2] If equal parts of KOH and o-nitro toluene are heated with one-half part of water on a water-bath for 5 hours the product will contain 22% anthranilic acid, 12-1/2%

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1. Berichte 13,290
2. Zeitschrift fur Angewandte Chemie 13, (1900)

o-toluidene, 4-1/2% unchanged o-nitro toluene, and 1% of ammonia will be evolved, percentages being calculated on the weight of o-nitro toluene at start. The toluidene and nitro-toluene are removed by steam distillation and the anthranilic extracted with ether or precipitated from a dilute acetic acid extract with copper acetate, the copper salt being afterwards decomposed by hydrogen sulfide. The above proportions seem to represent about the optimum conditions so far as the percentage of water is concerned. Doubling this quantity reduced the yield to 0.4%.

When 5 g. o-nitro toluene were mixed with 50 cc. of alcoholic potash and allowed to stand in the cold for eight months a small percentage of anthranilic acid was recovered from the solution. But when nitro toluene is heated on a water-bath with dry potash a violent exothermic reaction takes place and as above ammonia, toluidene, and anthranilic acid are formed together with much tar. Richter in his "Organischen Chemie" (1913) gives the following steps for the reaction between nitre-toluol and alkali liquors

(1)	(2)	(3)	(4)
o-nitro toluol	o-nitroso benzyl alcohol	anthranil	anthranilic acid

While the above changes are interesting from a theoretical standpoint, the low yields and the difficulties of separation and purification of the resulting product make them impractical commercially and the work was conducted along the lines of oxidation of the methyl group for the production of o-nitro benzoic acid which can then be reduced to anthranilic acid by any suitable means.

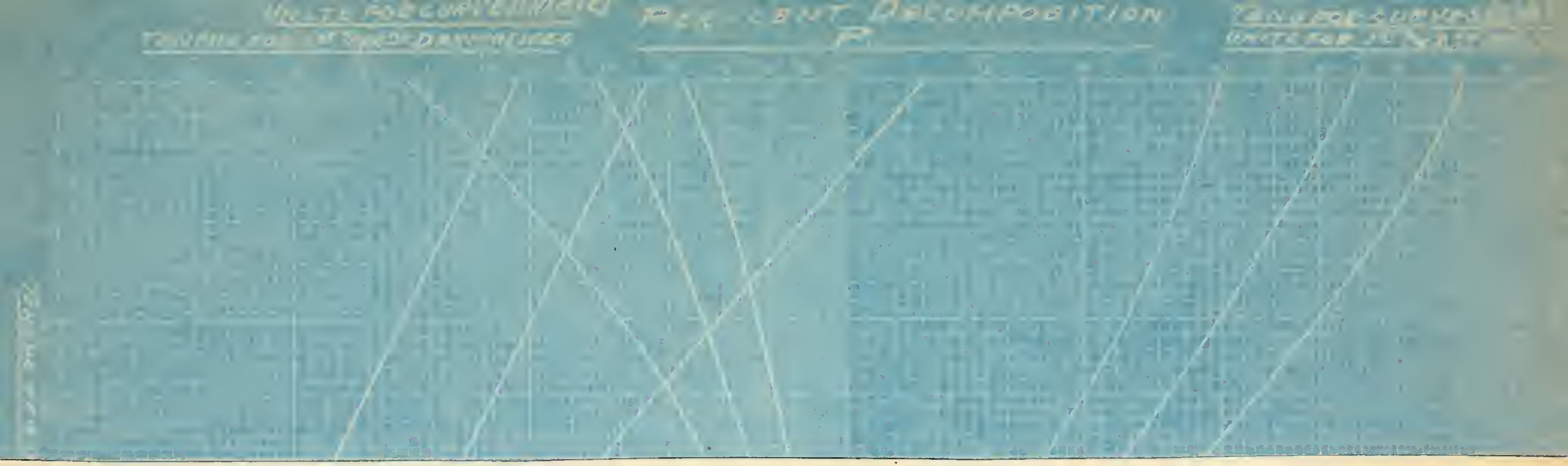
PRELIMINARY STUDY OF OXIDIZING AGENTS

Before beginning the actual work of oxidation it was decided to make a brief preliminary study of the behaviour of potassium permanganate when the oxidizable material was not present, it having been decided to use permanganate as the best oxidant for o-nitro toluol. This preliminary study was undertaken to determine, if possible, the effect of concentration and time of boiling on the rate of spontaneous decomposition of potassium permanganate in the presence of oxides of manganese. The material used analyzed 99% theoretical oxidizing value when titrated against sodium oxalate in sulfuric acid solution. In every case the permanganate was run into the oxalate heated to 60° to 70°, as this gave more concurrent results than the reverse titration.

The method in brief was as follows: The desired quantity of permanganate was weighed and accurately dissolved in 100 cc. of water and then boiled in a 250 cc. Erlenmeyer flask (with a little MnO_2) under a reflux condenser for the proper time. The flask was then removed, and the solution filtered with suction through a thick asbestos mat on a Buchner funnel which had previously been thoroughly washed

with permanganate. Care had to be taken to leave the surface of the mat undisturbed for MnO_2 had a tendency, otherwise, to pass through and could not be detected in the filtrate because of its deep color. After washing the asbestos with distilled water the filtrate and washings were placed in a volumetric flask and diluted to the mark. Aliquot portions were then titrated as above indicated. The difference between the result thus obtained and weight of permanganate used at start represents the quantity decomposed.

The solutions at the start were all neutral but developed some alkalinity as decomposition progressed. One half the final alkalinity in per cent KOH was assumed to be the average for the whole run (Table 1). These figures, while showing considerable irregularity, give a curve on ordinary cross-section paper approximately a rectangular hyperbola. When plotted on log-log paper, however, (Fig.) it will be seen at once from curves (A), (B), (C), which represent the original data, that the curves on cross-section paper are not strictly speaking hyperbolae. By the usual method of obtaining a straight



PER CENT DECOMPOSITION
P

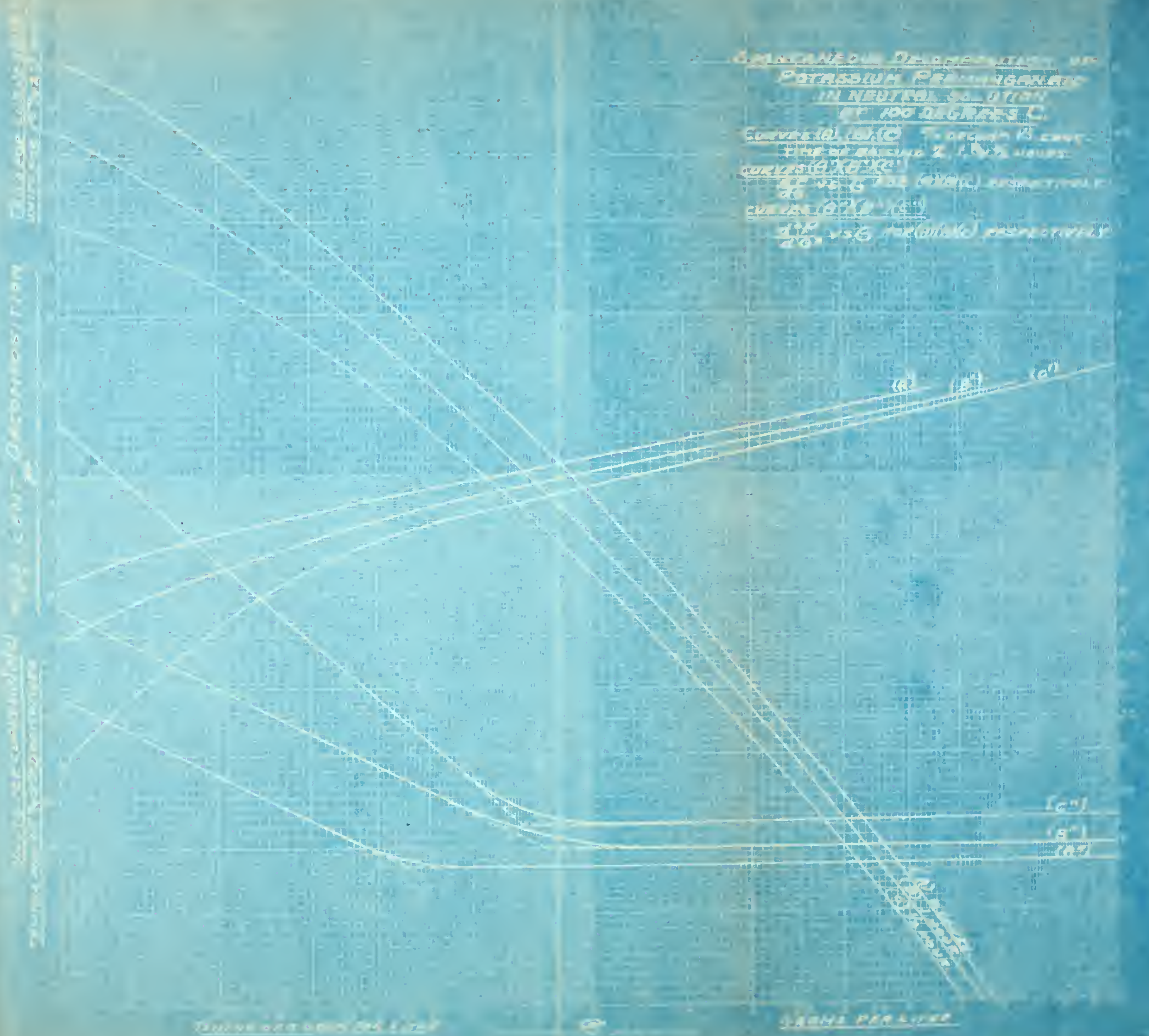

POTASSIUM PERMANGANATE
IN NEUTRAL SOLUTION
AT 100 DEGREES C
(a)
(b)
(c)
(a')
(b')
(c')

Fig A

TABLE 1

DECOMPOSITION OF PERMANGANATE

Volume of Solutions 100cc.

Time 1/2 Hour				Time 1 Hour			
Start	Finish	Diff.	Percent Decomp.	Start	Finish	Diff.	Percent Decomp.
5.000g	5.000g	.000g	0.00%	5.000g	5.000g	.000g	0.00%
2.000	1.985	.015	.75	3.000	3.000	.000	0.00
1.000	.995	.005	.50	2.000	1.980	.020	1.00
.600	.596	.004	.67	1.000	.996	.004	.40
.300	.294	.006	2.00	.600	.590	.010	1.67
.100	.0932	.0068	6.80	.300	.2876	.0124	4.14
.010	.0070	.0030	30.00				

Time 2 Hours			
Start	Finish	Diff.	Percent Decomp.
5.000g	4.930g	.070g	1.40%
.600	.596	.004	.67
.300	.2905	.0095	3.16
.100	.090	.01	10.00
.010	.0038	.0062	62.00

line from such a curve as (A), viz., by adding equal increments to the ordinates, the desired result was not obtained but a curve with an inflection point in the center. A straight line could be drawn through this approximating the results between certain limits and its equation obtained, but it seemed better to go on and attempt to get a real solution rather than an approximation. After trying many methods of attack a means was finally found. This consisted of getting the slope of curve (A), for instance, for each point and plotting this against G giving curve (A'), and then repeating this procedure upon (A') to give (A"), and similarly for curves (B), (B'), (B"), (C), (C') and (C"). The slopes in every case were obtained in the usual way; a line parallel to a tangent to the curve (at the point desired) is drawn through an origin and its ordinate, where it cuts the axis of ordination, divided by its abscissa. For any given line parallel to a tangent the slope is, say, $\frac{\log 12.1}{\log 10} = 1.082$. This figure is then plotted against the corresponding value of G (grams $KMnO_4$ per liter) to form the next higher derivation curve.

When a straight line was finally obtained in

the second derivative curve, the equation proved to be a transcendental one of a very complex order and was not fully worked out, both because of the difficulties of integration and because what work was done on it showed it to be so complex as to effectually hide the physical significance that was being sought for in the algebraic expression[1]. The presence of the extraordinarily sharp break in curves (A"), (B"), (C") is particularly interesting, the breaks lying as they do almost at the same point in the value of G and indicating a decided change in conditions. Throughout the entire possible range of concentrationsa decrease in concentration was accompanied by an increase in the per cent decomposition, the normal curve approximating, as has been said, a rectangular hyperbola, but deviating from it more and more rapidly as the concentration of $KMnO_4$ decreased as shown in (A), (B), (C), Fig.A. This deviation towards a somewhat lower percentage decomposition than that given by a true hyperbola is, however, uniform and could be expressed by a constant coefficient of G, that is $P_d = \frac{K}{G}$ where P_d is the actual deviation in percent decomposed from that given by a hyperbola. But when G reaches a value of

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[1] The writers wish to express their gratitude to Asst. Professor W.C. Krathwohl, PH.D. for his generosity of time and effort devoted to help and suggestions on the problem of integrating this logarithmic second differential expression.

from 0.45 to 0.80 grams per liter this simple expression no longer holds good; a sharp change and a definite and uniformly increasing coefficient is now required to replace K such that it shall vary inversely as G or as a power of G where that power is greater than unity.

The effect of time of boiling and concentration of $KMnO_4$ upon the decomposition of $KMnO_4$ in alkaline solution was also studied. The method of procedure was that previously described.

TABLE 2

Decomposition of $KMnO_4$ in Alkaline Solution
100 g. H_2O, 5 g. $KMnO_4$ and 1 g. NaOH

Time of Boiling (hours)	Start	Finish	Diff.	Per cent Decomp.
.25	5.00g	4.96g	.04g	0.8
.50	5.00	4.96	.04	0.8
1.00	5.00	4.94	.06	1.2
2.00	5.00	4.95	.05	1.0

TABLE 3

Decomposition of $KMnO_4$ in Alkaline Solution,
100 g. H_2O, 1g. NaO H, Time of Boiling 0.5 Hours

Start	Finish	Diff.	Per-cent Decomp.
5.00 g.	4.96 g.	.04 g.	0.8
4.00	4.93	.07	1.75
3.00	4.98	.02	0.66
2.00	4.98	.02	1.00
1.00	4.(99	.01	1.00

These data on the decomposition inthe presence of alkali indicate that the action of the alkali

is slightly to increase the rate of decomposition of the permanganate over that obtained in neutral solution but since the actual amount of decomposition is so slight as to be negligible as compared with that obtained in the presence of an oxidizable body the experiments were not carried to a sufficiently low concentration of $KMnO_4$ to show the characteristics developed in neutral solution though, no doubt, these same characteristics were present. In general these results bear out thos previously obtained and seem to indicate that the effect of the duration of boiling is similar whether the solution is neutral or alkaline.

The foregoing is merely a general description and makes no pretense of being an interpretation of them. What the physical significance of the apparently increased stability below .60g per liter as compared with the stability at concentrations above that is, we do not pretend to say. We merely indicate that such is the case. As to applying the information gained in this study to the actual oxidation, by making allowance for the rate of spontaneous decomposition of the permanganate, it did not seem practical to do so; first because the average concentration of permanganate maintained

in the oxidizing solution is unknown and, second, because the actual quantity decomposed per hour is insignificant compared to that reduced by oxidation of the organic body to be acted upon.

OXIDATION OF O-NITRO TOLUENE

The raw nitro-body was obtained from the Newport Company of Carrollville, Wis., and from the brief tests made seemed to be of exceptional purity. The only isomer customarily present is the para-compound and this with two parts of the ortho-body forms an entectic mixture freezing at -15.2°, whereas the two isomers alone freeze at 54.4° and -10.5° respectively. The equilibrium diagram given in Landolt and Bornstein is:

Per cent P.N.T.	Solid Phase	Temperature
100.0	P.N.T.	54.4°
91.6	"	46.2
79.0	"	38.5
67.5	"	30.4
46.6	"	11.6
37.2	"	-1.2
30.5	Entectic O.N.T.-P.N.T.	-15.2
24.9	O.N.T.	-14.4
16.3	"	-12.1
11.2	"	-11.3
0.0	"	-10.5

On slow cooling our raw material did not freeze at -10.5° but this was found to be due to supercooling, because when a few crystals of a

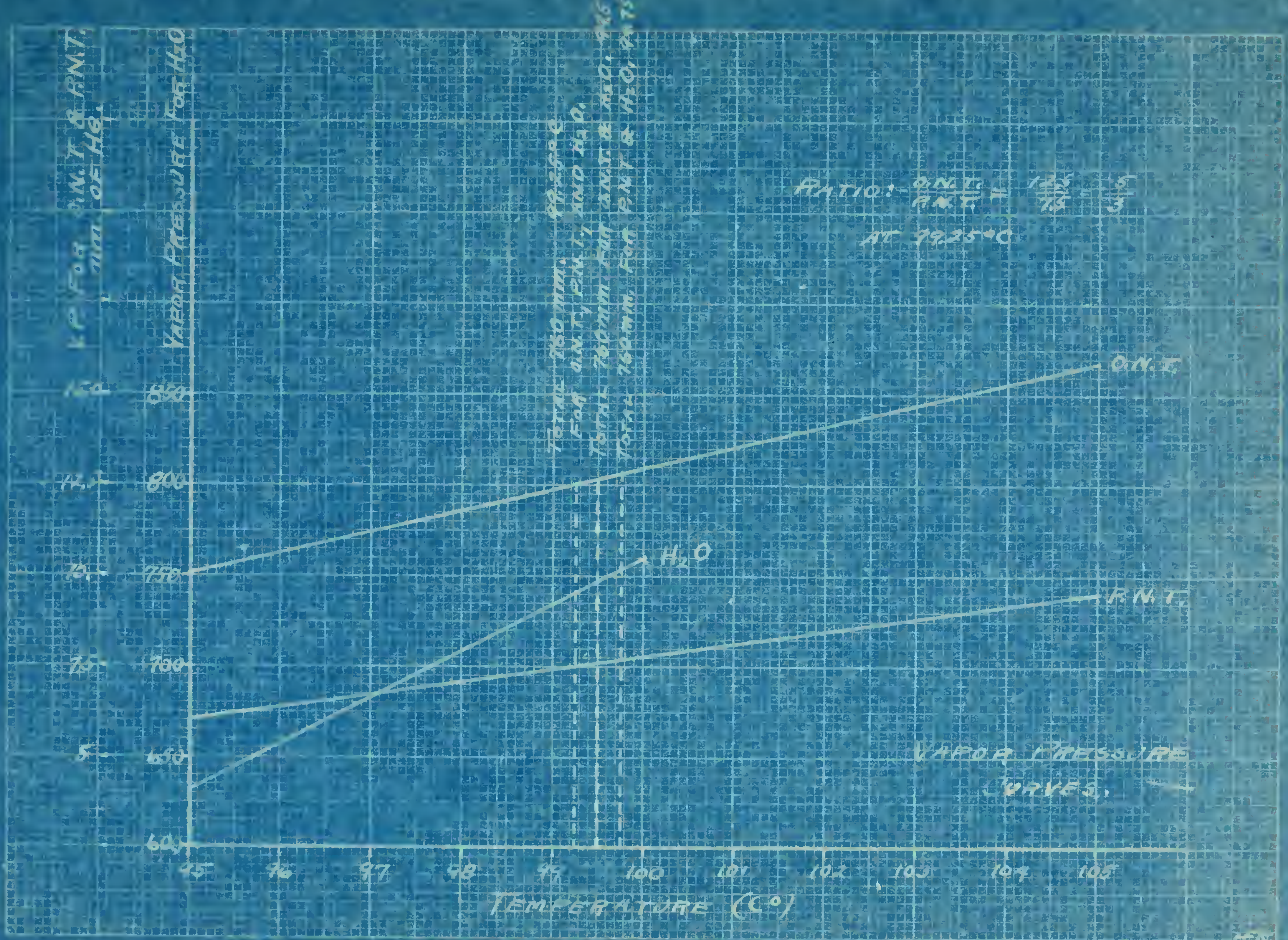
V.P. FOR O.N.T. & P.N.T. mm. OF HG.
VAPOR PRESSURE FOR H₂O
15.
12.5
10.
7.5
5.
850
800
750
700
650
600
95
96
97
98
99
100
101
102
103
104
105
TEMPERATURE (C°)
TOTAL 760 mm. 99.25°C
FOR O.N.T., P.N.T., AND H₂O.
TOTAL 760mm. FOR O.N.T. & H₂O. 99.5°
TOTAL 760mm. FOR P.N.T. & H₂O, 99.75°
RATIO: O.N.T./P.N.T. = 125/75 = 5/3
AT 99.25°C
O.N.T.
H₂O
P.N.T.
VAPOR PRESSURE CURVES.

FIG. B.

previously frozen sample were dropped into the liquid cooled to -10.5° solid matter began at once to separate and continued to do so until the whole mass had solidified, the temperature meanwhile remaining stationary. This indicated that by far the larger part of the material was o-nitro toluene as any appreciable admixture of other isomers would have lowered the freezing point appreciably.

Next about 500 cc. of the raw material were cooled and sufficient solid o-nitro toluene filtered off to make 200 cc. when melted. Steam distillation was not applicable for further purification as it will be seen by a reference to Fig. B that three parts of the para compound would distil over with every five parts of the ortho, so as a final check on the purity a distillation was made on this purified product. The distillation curve so obtained is shown in Fig. C. The thermometer used was calibrated by the Bureau of Standards and all temperatures were corrected for calibration, emergent stem, and barometric pressure to 760 mm.

With this purified material a specific gravity determination and an index of refraction were also

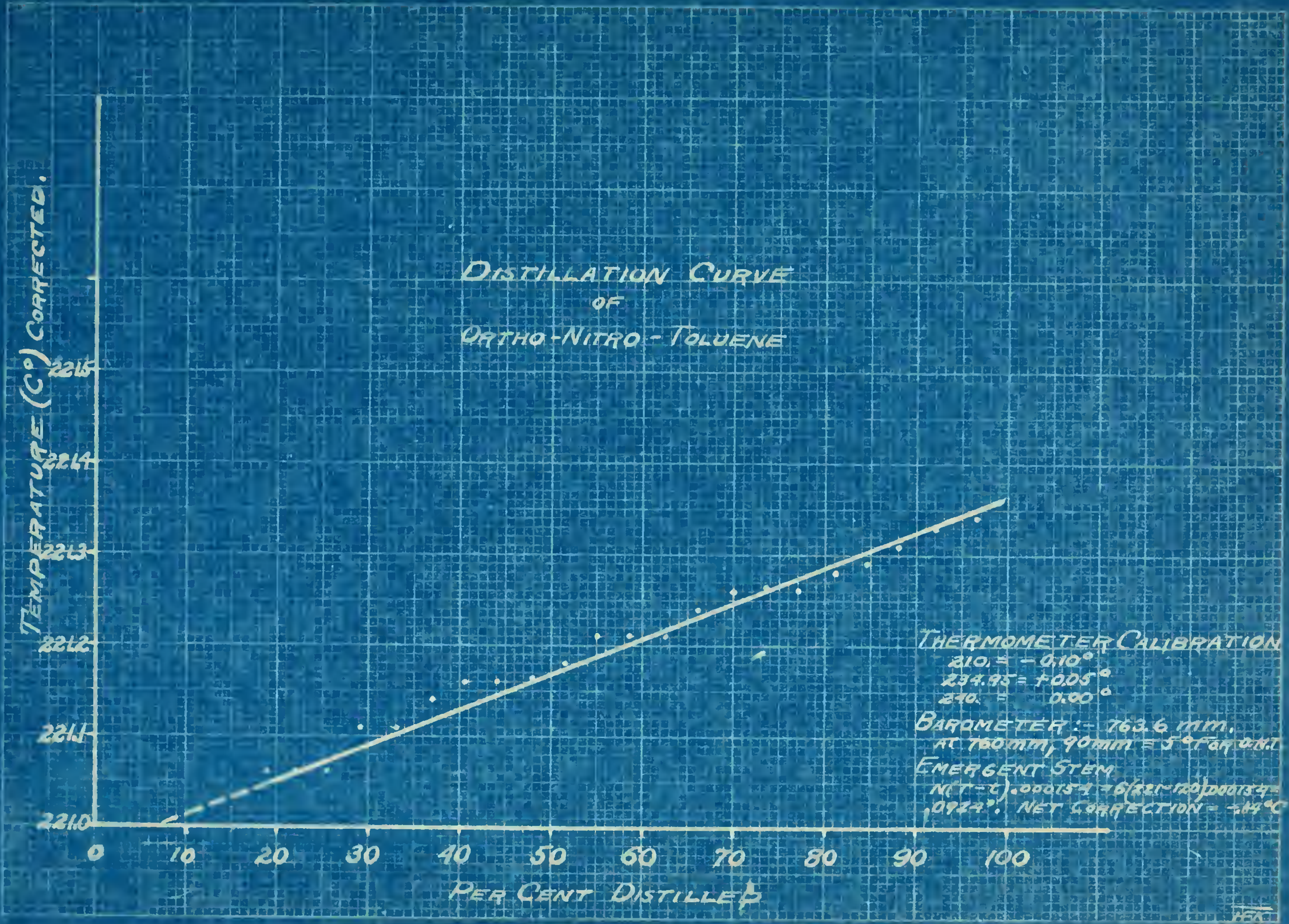
DISTILLATION CURVE
OF
ORTHO-NITRO-TOLUENE
TEMPERATURE (C°) CORRECTED.
221.5
221.4
221.3
221.2
221.1
221.0
0
10
20
30
40
50
60
70
80
90
100
PER CENT DISTILLED
THERMOMETER CALIBRATION
210. = −0.10°
234.95 = +0.05°
240. = 0.00°
BAROMETER :- 763.6 mm.
AT 760mm, 90mm = 5°For O.N.T
EMERGENT STEM
N(T−t).000154 = 6(221−120).000154 =
.0924°. NET CORRECTION = −.14°C

FIG. C.

made and these physical constants for what is probably the purest sample of this material ever studied are herewith appended. The oil was in every case dried over calcium chloride before being used.

Sp. g............................ $1.2031\frac{20^\circ}{4}$

$1.1641\frac{20^\circ}{15^\circ}$

Refractive index at 20°............. 1.659

Boiling point at 360 mm.(Corr.)..... 221.3°

The potassium permanganate used was of the commercial variety and where titrated against pure sodium oxalate it ran 99% of theoretical oxidizing power. The sodium hydroxide analyzed

86% NaOH
3% Na_2CO_3
2% Na Cl
7% Na_2SO_4
2% H_2O

All weights of hydroxide recorded are for the crude material and may be considered to be approximately 90% NaOH since any Na_2CO_3 is as effective as NaOH after a short time due to the CO_2 liberated by over oxidation. The nitric acid, potassium ferricyanide, and sodium and potassium dichromate were not analyzed nor studied particularly as they did not appear especially useful in this work.

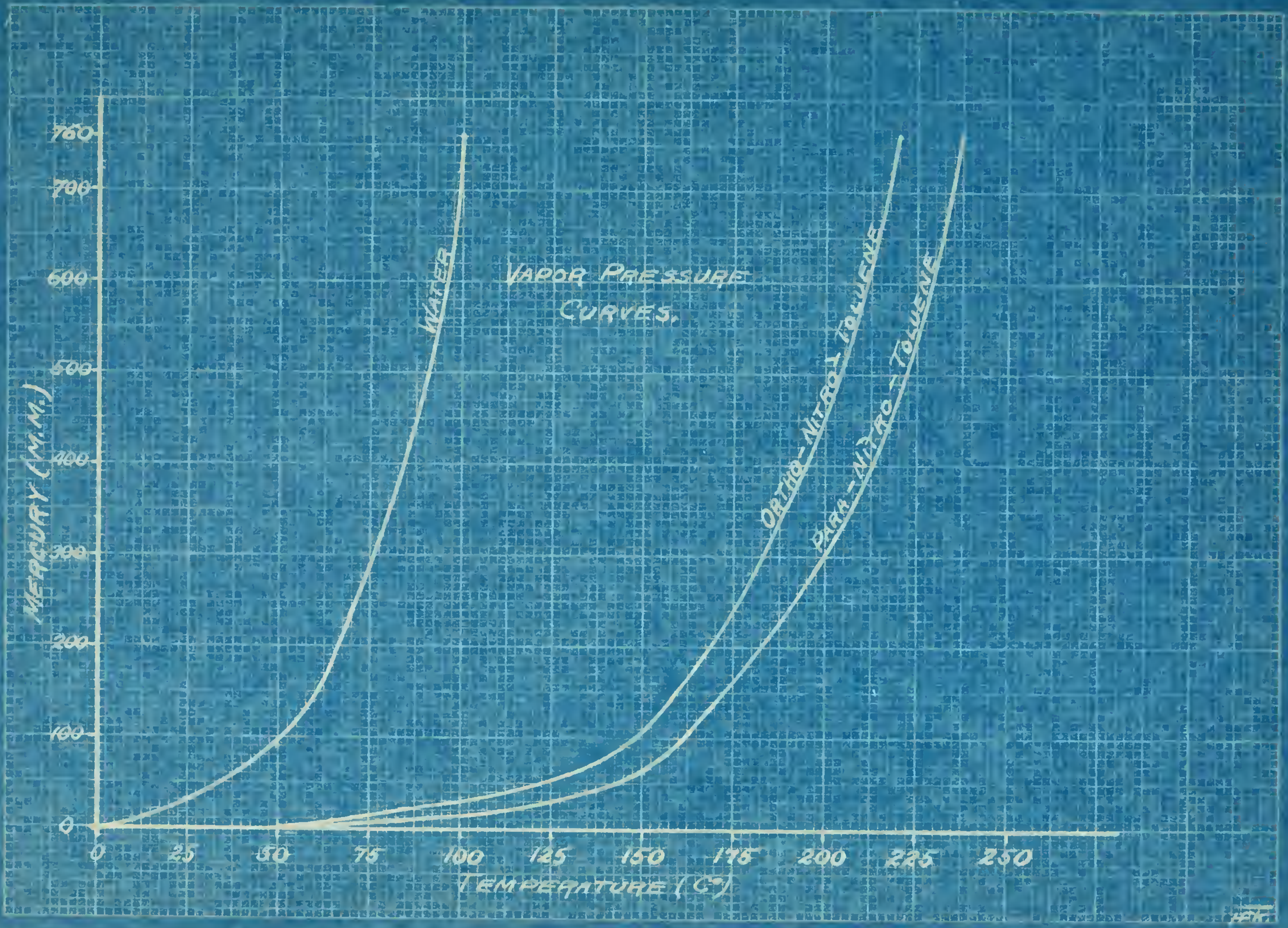
VAPOR PRESSURE
CURVES.
WATER
ORTHO-NITRO-TOLUENE
PARA-NITRO-TOLUENE
MERCURY (M.M.)
760
700
600
500
400
300
200
100
0
0
25
50
75
100
125
150
175
200
225
250
TEMPERATURE (C°)

FIG. D.

The apparatus in every case consisted of a wide-mouthed, round-bottomed flask equipped with a Hopkins reflux condenser and the cork protected with lead foil. This was entirely suitable for all reagents except nitric acid which tended to destroy all connections and necessitated the use of ground glass joints. Steam distillation was conducted in the usual way and the manganese dioxide filtered off on a Buchner funnel.

The oxidation of o-nitro toluene to o-nitro benzoic acid was tried with the following oxidizing agents: potassium ferricyanide, potassium dichromate, sodium dichromate, concentrated nitric acid and potassium permanganate.

The oxidation of o-nitro toluene with potassium ferricyanide was carried on in an alkaline solution. Sodium hydroxide was used in place of potassium hydroxide. The following is an account of the method used.

[1]Fifty grams of potassium ferricyanide and 23 grams of KOH were dissolved in 200 ccs. of hot water and 2 grams of o-nitro toluene were added. This was boiled for 2 or 3 hours in a flask fitted with a reflux condenser. The unoxidized

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[1] Berichte 16-1883-P.52

o-nitro toluene was removed by steam distillation. The iron oxide precipitate was filtered off and the filtrate was acidified with hydrochloric acid. The filtrate was extracted with ether and the etheral solution evaporated. The reside is o-nitro benzoic acid.

Two oxidations were made with potassium ferricyanide in sodium hydroxide solution with the following results.

No.	Potassium Ferricyanide g.	Sodium Hydroxide g.	Water, G.
1.	50. (47% excess)	25	200
2.	37.4 (10% excess)	20	200

No.	O-Nitro Toluene g.	O-Nitro Tol. Recovered g.	Per cent yield of O.N.B.
1.	2.00	.01	38.20
2.	2.00	.02	30.00

Altho it is possible to oxidize o-nitro toluene with potassium ferricyanide in alkaline solution, the results obtained were not very satisfactory. The product obtained was gray in color and the yields were low. The large amount of potassium ferricyanide needed per unit weight of o-nitro benzoic acid formed, together with the large excess required, make the method a costly one. Assuming a yield of o-nitro benzoic acid of 50%,

with a 50% excess of potassium ferricyanide, 42 pounds of potassium ferricyanide are required for every pound of o-nitro benzoic acid formed. The presence of iron salts discolors the o-nitro benzoic acid formed giving it a gray color.

It was not possible to oxidize o-nitro toluene to o-nitro benzoic acid with potassium dichromate in sulfuric acid solution. One run was made with the following result.

Potassium Dichromate, g.	Sulfuric Acid, g.	Water, g.
27.5	46.0	200

O-Nitro Toluene, g.	O-Nitro Toluene Recovered, g.	Per cent yield of O.N.B.
11.65	10.09	0.00

This charge was boiled for 3-1/2 hours in a flask fitted with a reflux condenser and no o-nitro benzoic acid was formed. The amount of o-nitro toluene recovered was almost equal to the amount used at the start. This result confirms the statements in the literature, which say that the ortho compound cannot be oxidized by a chromic acid mixture.

Sodium dichromate in hydrochloric acid was also tried as a possible oxidizing agent. Two

runs were made with the formation of no o-nitro benzoic acid. In Run No. 1, the charge was boiled for 1-1/2 hours and in Run No. 2 the charge was boiled for 8 hours.

No.	Sodium Dichromate g.	Hydrochloric Acid, g.	Water, g.
1.	27	22	500
2.	27	11	200

O-Nitro	Toluene, g.	O-Nitro Toluene Recovered g.	Per cent Yield of O.N.B.
1.	11.65	9.88	0.00
2.	11.65	8.81	0.00

Concentrated nitric acid was used as the oxidizing agent with no success. The absence of o-nitro benzoic acid may be due to insufficient boiling, for it has been obtained by boiling o-nitro toluene for 40 hours or more with concentrated HNO_3. The maximum time of boiling was 3 hours as it did not seem practical to boil longer than this. In Run No. 1 the charge was boiled for 2 hours. In Run No. 2 the time of boiling was 3 hours.

No.	Nitric Acid, g.	Water, g.	O-Nitro Tol., g.
1.	125	50	46.50
2/	100	25	23.25

No.	O-Nitro Toluene Recovered, g.	Per cent yield of O.N.B.
1.	26.06	0.00
2.	19.83	0.00

The fact that a large percentage of the o-nitro toluene was used up in the reaction without the formation of o-nitrobenzoic raises the question of what became of it. The o-nitro toluene was probably converted to di-nitro toluene by the action of the nitric acid, the nitric acid nitrating instead of oxidizing.

OXIDATION WITH PERMANGANATE

The best method pf procedure as finally determined was as follows: The proper amount of water containing the dissolved alkali was placed in the flask and the 30 g. o-nitro toluene run in from a pipette which was calibfated to deliver that weight. The requisite quantity of permanganate was then weighed out and introduced into the flask in about six portions at three-quarter-hour intervals and the mixture boiled with sufficient vigor to maintain a good stirring action. When completely decolorized after the last addition of permanganate. the flask was disconnected and set up for steam distillation while hot and there subjected to vigorous action

to remove all traces of unoxidized o-nitro toluol from solution and from the voluminous manganese precipitate. After the condensate becomes clear and the solution no longer smells of nitro toluol, the manganese-dioxide is filtered off and the filtrate acidified and evaporated to 500 cc., cooled, and o-nitro benzoic acid filtered off, dried at 100°, and weighed.

At this point it would be well to explain that allowance was made for the product remaining in solution when calculating the yield and, in order to determine the conditions at which this loss would be at a minimum, solubility curves were run for o-nitro benzoic acid against temperature and against the weight of chlorides present in a dilute hydrochloric acid solution, and also against temperature in dilute nitric acid (see Figs. E, F, and G.)

The solubility of o-nitro benzoic acid in a KCl-NaCl solution, acid with HCl is about 0.6% at 11° C. In order to determine whether the amount of O.N.B. left in solution could be conveniently

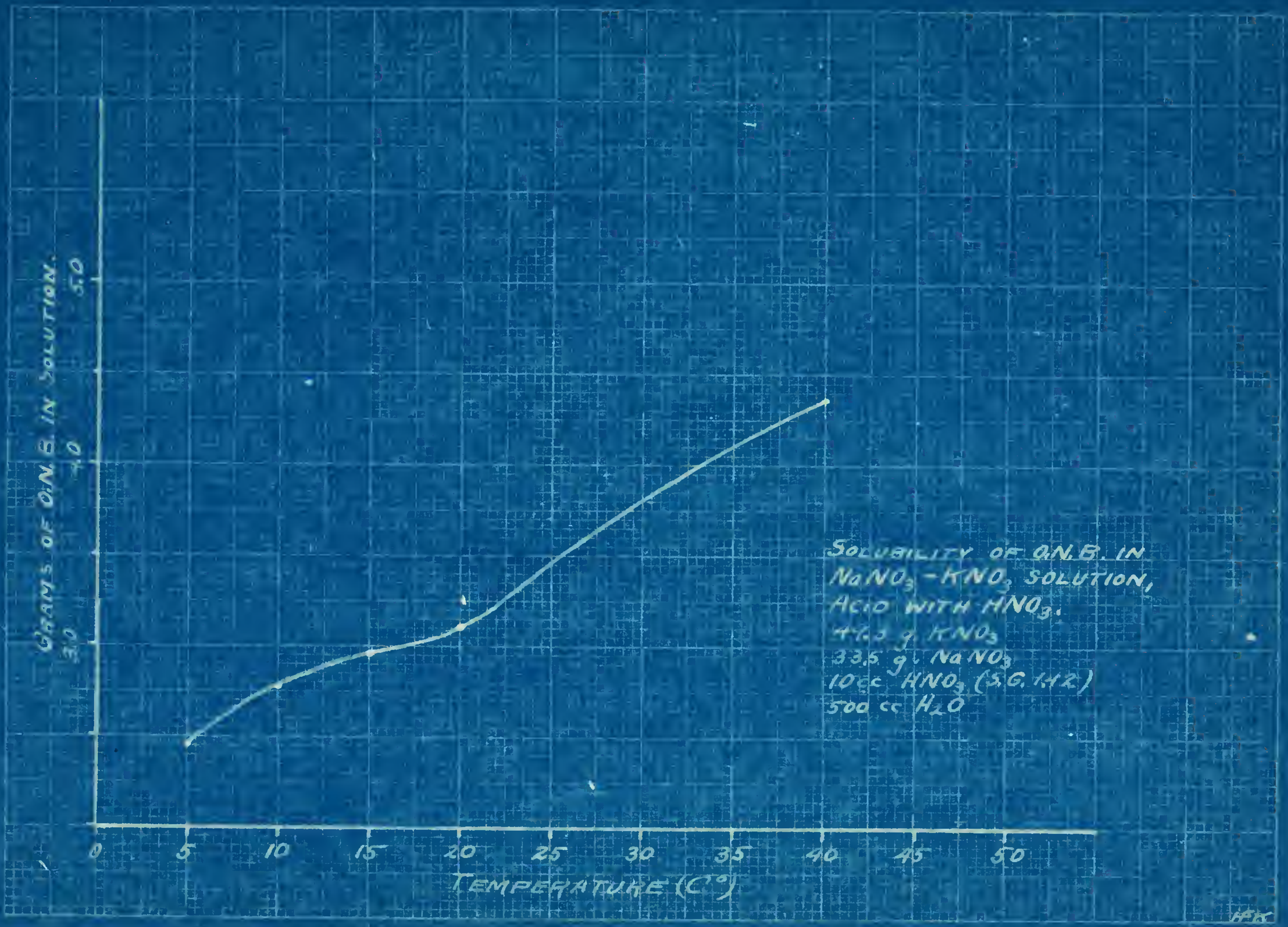
SOLUBILITY OF O.N.B. IN
$NaNO_3$-KNO_3 SOLUTION,
ACID WITH HNO_3.
[illegible] g. KNO_3
33.5 g. $NaNO_3$
10 cc HNO_3 (S.G. 1.42)
500 cc H_2O
GRAMS OF O.N.B. IN SOLUTION.
3.0
4.0
5.0
0
5
10
15
20
25
30
35
40
45
50
TEMPERATURE (C°)
HPK

FIG. E.

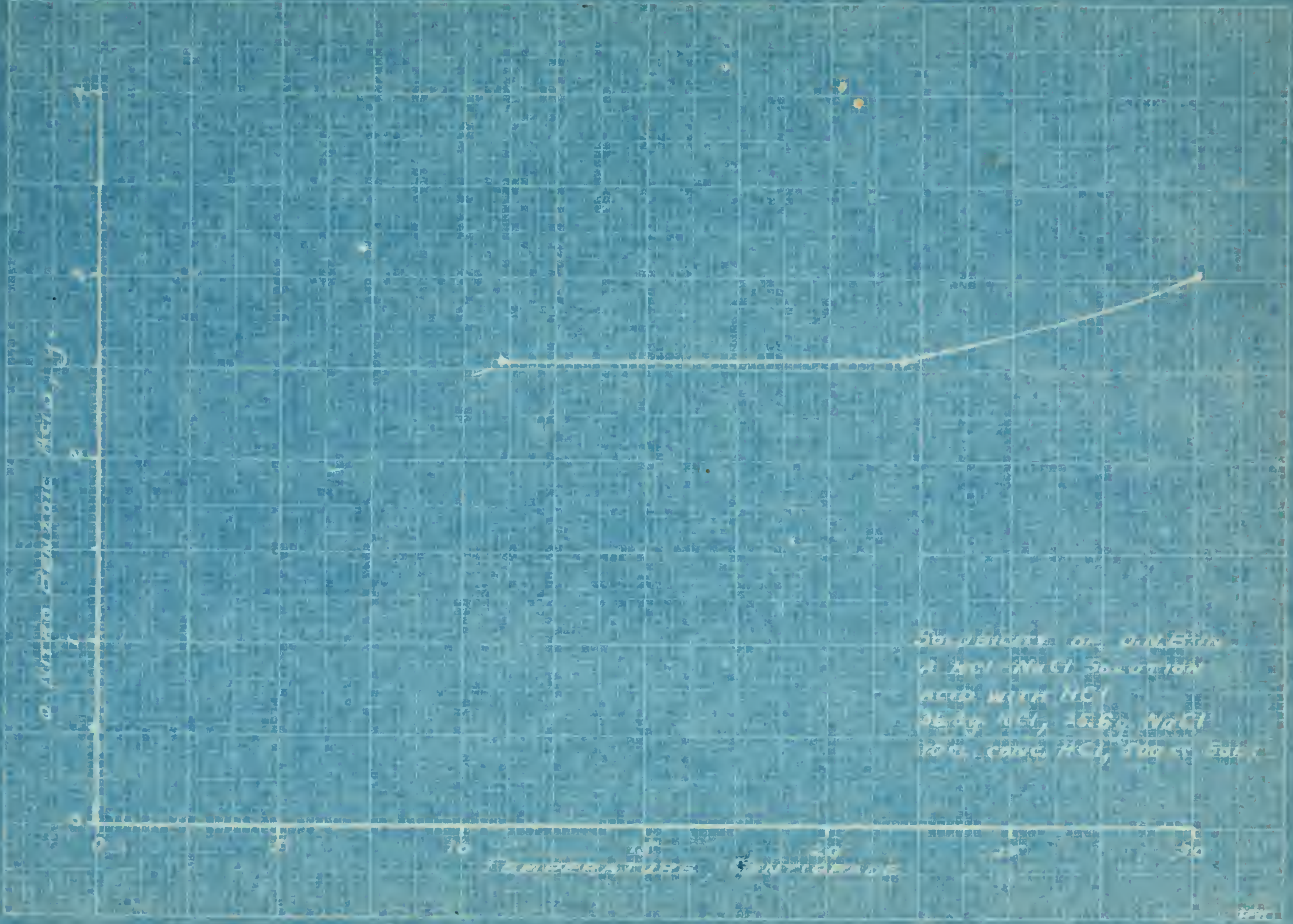
0
5
10
15
20
25
30
Temperature Centigrade
Solubility of
[illegible] NaCl Solution
acid with HCl
[illegible] HCl, 10.5g NaCl
10 cc. conc HCl, 100 cc. sol.

FIG. F

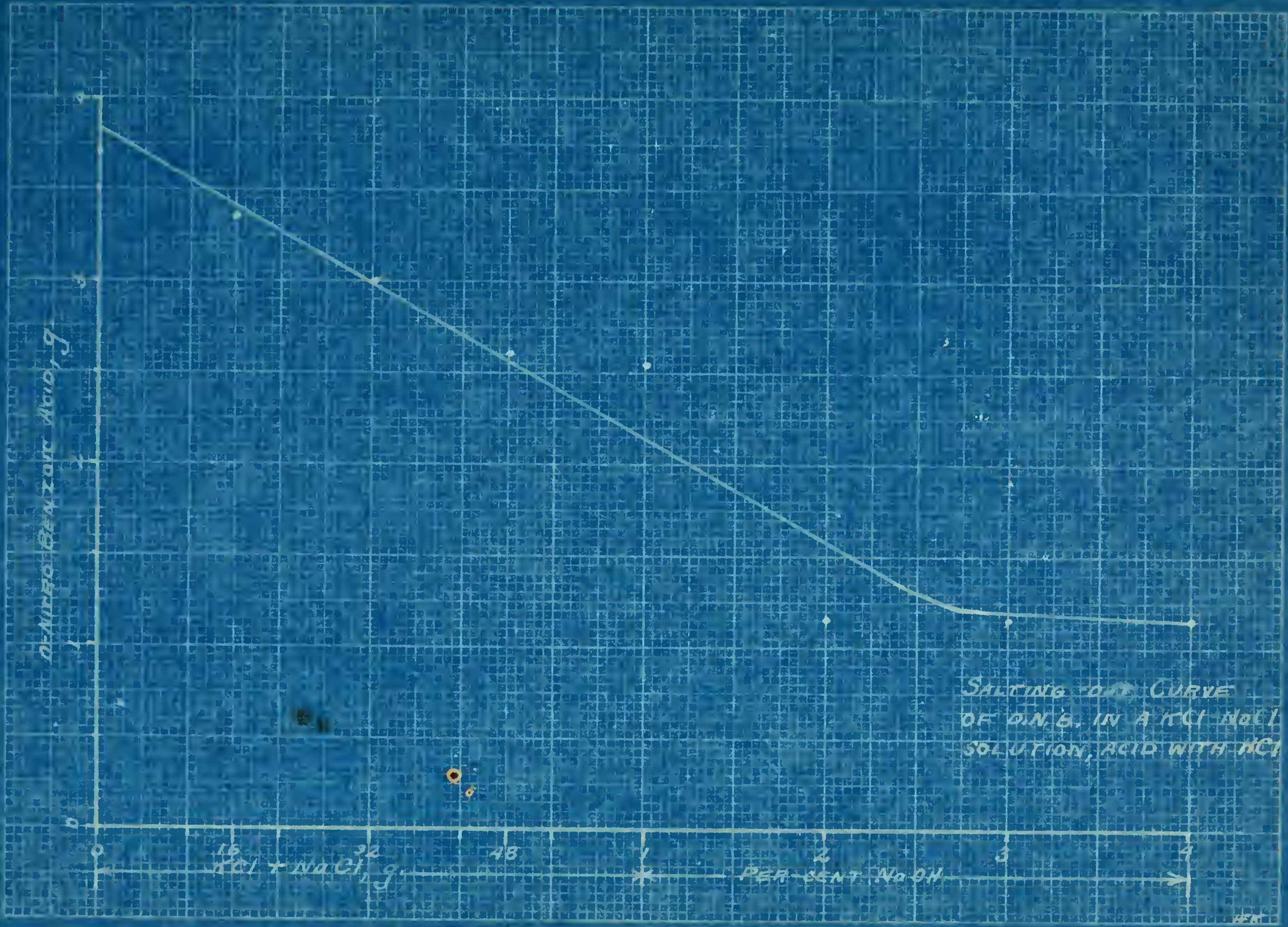
SALTING OUT CURVE
OF D.N.B. IN A KCl NaCl
SOLUTION, ACID WITH HCl
DINITRO BENZOIC ACID, g
0
1
2
3
4
0
16
32
48
KCl + NaCl, g.
1
2
3
4
PER CENT NaOH

FIG. 6.

lowered, some solubility determinations were made.

Besides hydrochloric acid, nitric, acetic and sulfuric acids were considered as possible acidifying agents. Owing to the low solubilities of the sulfates of potassium and sodium, sulfuric acid was eliminated as being undesirable for use.

Acetic acid was found undesirable as the acidifying agent because the solubility of O.N.B. in a $KC_2H_3O_2$-$NaC_2H_3O_2 \cdot 3H_2O$ solution, acid with $C_2H_4O_2$ was greater than 0.6% at 11° C. The $KC_2H_3O_2$ added to 500 cc. of H_2O was an amount equivalent to the K_2O resulting from the decomposition of the $KMnO_4$. The amount of $NaC_2H_3O_2 \cdot 3H_2O$ added to this same volume of H_2O was equivalent to the NaOH added with the $KMnO_4$ (1% of NaOH in 1750 cc. of H_2O.) The K_2O resulting from 77 g. of $KMnO_4$ was considered as this amount of $KMnO_4$ was added to each 30 g. of o-nitro toluene. 10 cc. of glacial $C_2H_4O_2$ was added to the solution.

Nitric acid was next considered. The solubility of O.N.B. in a KNO_3 - $NaNO_3$ solution acid with HNO_3 was found to be less than 0.6%

at 11° C. The actual figure is .56% at 11° C. at 5° C, the solubility drops to .49%.

The solubility curve of O.N.B. in the KNO_3-$NaNO_3$ solution acid with HNO_3 was determined as follows:

An amount of KNO_3 equivalent to the K_2O resulting from the decomposition of 77 g. of $KMnO_4$ was added to some water, which contained 10 cc. of concentrated HNO_3. An amount of $NaNO_3$ equivalent to the NaOH added with the $KMnO_4$ was added to this same solution. To this 5 g. of O.N.B. was added and the whole solution was made up to 500 cc. The O.N.B. added had a melting point of 147.7° C. The solution was warmed until most of the O.N.B. had dissolved. It was cooled to 40° C and the undissolved O.N.B. was filtered off. The residue was washed with some of the filtrate and was then dried. The filtrate was now cooled to 20° and the O.N.B. was filtered off and washed. Points on the curve were also obtained at 15, 10 and 5° C, similarly. The dried residues were treated with ether and the solutions were filtered, the filtrates being collected in weighed beakers.

The ether was evaporated and the remaining O.N.B. was weighed. This treatment with ether will separate the O.N.B. from any nitrates which might be present.

In order to correct the various yields of O.N.B. for the amount left in solution after crystallization, two solubility curves were determined. One curve gives the solubility of O.N.B. in a KCl-NaCl solution, acid with HCl, at various temperatures. The KCl in solution is equivalent to 77 g. of $KMnO_4$ and the NaCl is equivalent to the 1% of NaOH added. The other curve gives the solubility of O.N.B. in a KCl-NaCl solution, and with HCl at 15° C with various amounts of NaCl, the amount of NaCl added increasing up to the equivalent of 4%NaOH.

TABLE 4

Solubility of O.N.B. in a KCl-NaCl Solution Acid with HCl at various temperatures, 36.3 g. KCl, 25.6 g. NaCl

10 cc. conc. HCl, 500 cc. of Solution

Temperature C.	O.N.B. in solution, g.
11	2.54
22	2.55
30	3.02

TABLE 5

Solubility of O.N.B. in a KCl-NaCl Solution Acid with HCl at 15° C, with increasing concentrations of NaCl. 10 cc. Conc. HCl, 500 cc. of solution.

KCl,g.	NaCl,g.	$KMnO_4$ Equiv.,g.	NaOH Equiv.,g.	Per Cent	O.N.B. in Solution,g.
0.00	0.00	0.00	0.00	.00	3.70
9.40	6.60	19.95	4.50	.25	3.35
18.20	12.80	38.60	8.75	.50	3.00
27.00	19.00	57.30	13.00	.75	2.60
36.30	25.60	77.00	17.50	1.00	2.55
36.30	51.20	77.00	35.00	2.00	1.15
36.30	76.80	77.00	52.50	3.00	1.15
36.30	102.40	77.00	70.00	4.00	1.15

The solubility curve of O.N.B. in the KCl-NaCl solution, acid with HCl, was obtained in the same manner as the corresponding solubility curve of O.N.B. in the acid nitrate solution.

The salting out curve, which gives the solubility of O.N.B. for increasing concentrations of alkali, was obtained as follows:

An amount of KCl equivalent to 77 g. of $KMnO_4$ was mixed with an amount of NaCl equivalent to 17.5 g. of NaOH. This was divided into four equal portions and each portion was added to a 500 cc. HCl solution which contained 5 g. of o-nitro benzoic acid. The O.N.B. which separated from the solution after each addition of KCl-NaCl mixture was filtered off and weighed. After the

addition of the fourth portion, NaCl was added in successive amounts equivalent to 17.5 g. of NaOH. After each addition of NaCl, the O.N.B. which separated was filtered from the solution. The NaCl was added until an amount equivalent to 4% of NaOH was in solution. All the OLN.B. which was filtered from the solution was dried and treated with ether. The ether solution was evaporated in a weighed beaker and the amount of O.N.B. determined. By subtracting the total amount of O.N.B. separating at a definite concentration of NaCl from 5 grams, the amount left in solution at that concentration is determined.

In the use of potassium permanganate in alkaline solution there are three possible factors to be taken into account in determining the optimum conditions for the oxidation; these are concentration of reacting substances where their proportions to one another is kept constant, concentration of alkali, and per cent of permanganate in excess of theoretical.

EFFECT OF CONCENTRATION

This was determined by arbitrarily selecting

an alkalinity and a certain excess of $KMnO_4$ and varying the amount of water used with a given weight of o-nitro toluol. Brief preliminary experiments lead us to think that a concentration of 1% alkali and 10% excess permanganate would be an approximation to optimum conditions and would be sufficiently close for determining optimum dilution. This supposition was afterwards shown to be correct as we found that the use of a different alkalinity or a different excess of permanganate gave essentially the same shaped curve for yield vs. dilution, though of course in a different vertical position on the cross-section paper. This showed that an optimum dilution obtained from one arbitrarily chosen set of conditions held for others and this, in general, is true for optima of alkalinity and of per cent excess permanganate.

All figures are based on 30 g. of o-nitro toluol and will be so understood in the following discussions unless otherwise specified. Increasing the quantity of water from zero up to 1-1/2 to 1-3/4 liters produces a marked increase in yield, but beyond a diluting of

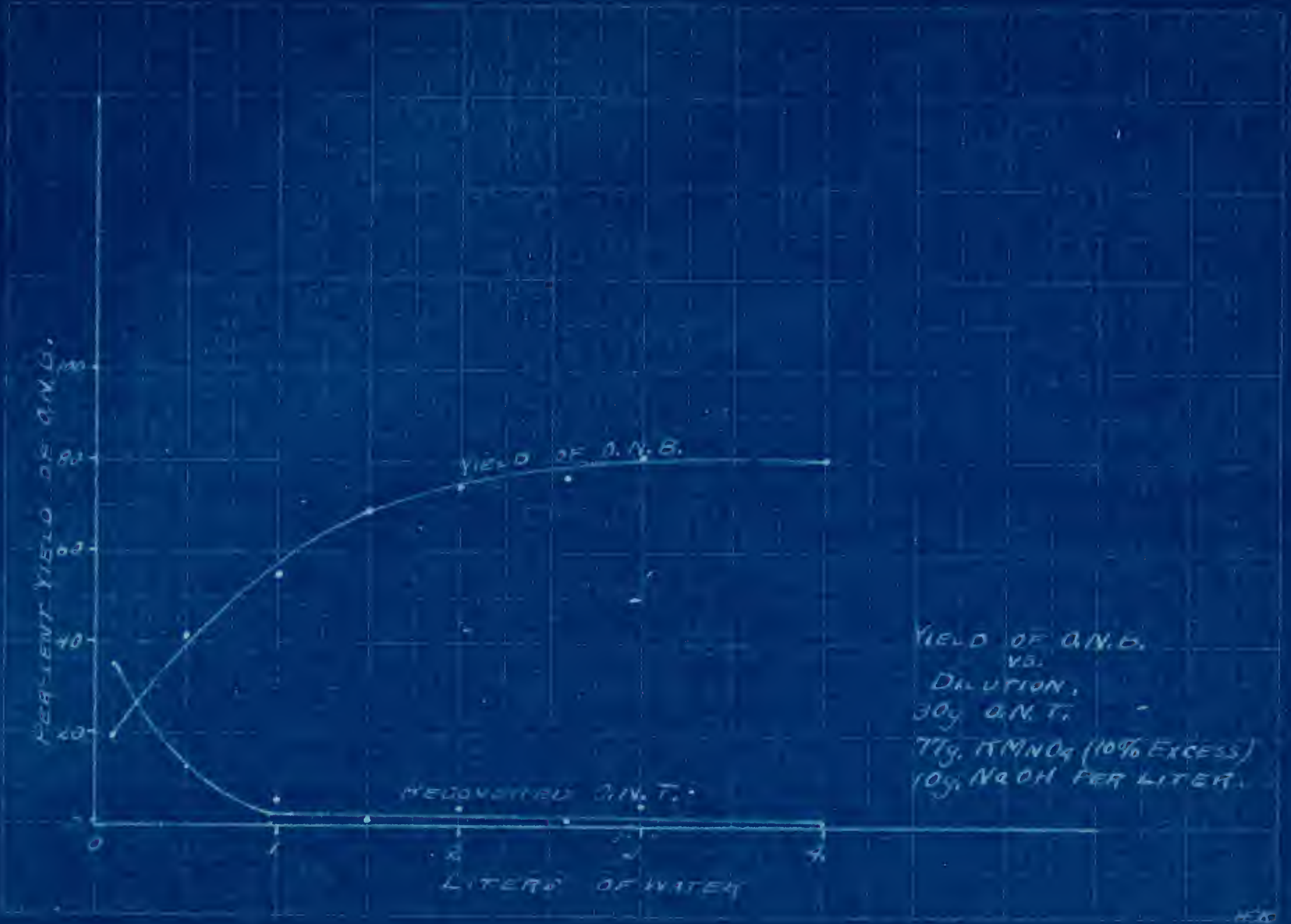
PER CENT YIELD OF O.N.B.
100
80
60
40
20
0
1
2
3
4
LITERS OF WATER
YIELD OF O.N.B.
RECOVERED O.N.T.
YIELD OF O.N.B.
VS.
DILUTION.
30g. O.N.T.
77g. KMnO4 (10% EXCESS)
10g. NaOH PER LITER.

FIG. H.

2 liters the curve (Fig.H) begins to flatten out and, although it continues to rise slightly, does not show an increase in yield of over 6% when the dilution is increased from 2 liters to 4 liters. The dilution to select is quite optional and in commercial work should be governed by the cost considerations of water, steam, space, capacity of equipment, and value of raw material and product.

Per cent yield of o-Nitro Benzoic Acid vs. Dilution, 30 g. of O.N.T., 77 g. of $KMnO_4$ (10% excess) and 10 g. NaOH per liter of Water

Water, cc.	O.N.T. Recovered, g.	Per cent	Yield of O.N.B., g.	Per Cent
100	10.71	35.70	7.23	19.75
500	3.77	12.56	15.23	41.70
1000	1.73	5.77	20.12	55.00
1500	0.48	1.60	25.20	68.80
2000	1.15	3.84	27.14	74.20
2575	.30	1.00	27.82	76.10
3000	1.38	4.60	29.52	80.70
4000	0.103	0.34	29.36	80.20

EFFECT OF ALKALI

The conditions for determining this variable were chosen in a manner similar to those used for determining the effect of dilution except that in this case we used a dilution which our previous work showed to be an optimum. This was

taken at 1750 cc. which seemed best as a point at which a reasonable dilution was accompanied by fairly high yields. The quantity of o-nitro toluene used was still held at 30 g. and the permanganate at 10% in excess of theoretical while the alkalinity was varied from zero to 8% by weight of solution. (By alkalinity we refer here to the sodium hydroxide - 90% NaOH - actually added and make no reference to the potassium hydroxide formed by decomposition of the permanganate as this is a constant quantity.) The effect of varying amounts of alkali added does not produce a very large change in the percentage of nitro toluene oxidized for two reasons. The 27.3 g. of KOH formed from 77 g. of permanganate may be said to represent an average alkalinity throughout the run of 13.7 g. or an equivalent of 0.6% in terms of NaOH, and this as well as the caustic that is added is reduced in effectiveness by the CO_2 evolved during oxidation. As a matter of fact it was found that in every case up to 7% alkalinity considerable quantities of CO_2 were given off which showed that all the alkali was present as

carbonate and the only alkalinity being dealt with was that due to hydrolysis of potassium and sodium carbonates. This was quite conclusively proved in two ways. In one or two runs escaping CO_2 was caught in standard barium hydroxide solution and the excess hydroxide titrated with standard acid; the caustic present in the oxidizing solution was calculated as carbonate and the total CO_2 thus obtained figured to o-nitro toluol. This added to the unchanged O.N.T. and to that which was converted to o-nitro benzoic acid added up to over 99% of the O.N.T. at the start. Next a run was made in which equivalent weight of sodium carbonate was substituted for the usual caustic soda keeping everything else the same. The product thus obtained was almost identical in quantity, purity, and appearance with that formerly gotten, the only difference in the two runs being that a vastly greater amount of CO_2, as would be expected, was evolved.

The time for oxidation was nearly the same in all cases where alkali was used, but where none was added the action required about 50% more time to go to completion. The appear-

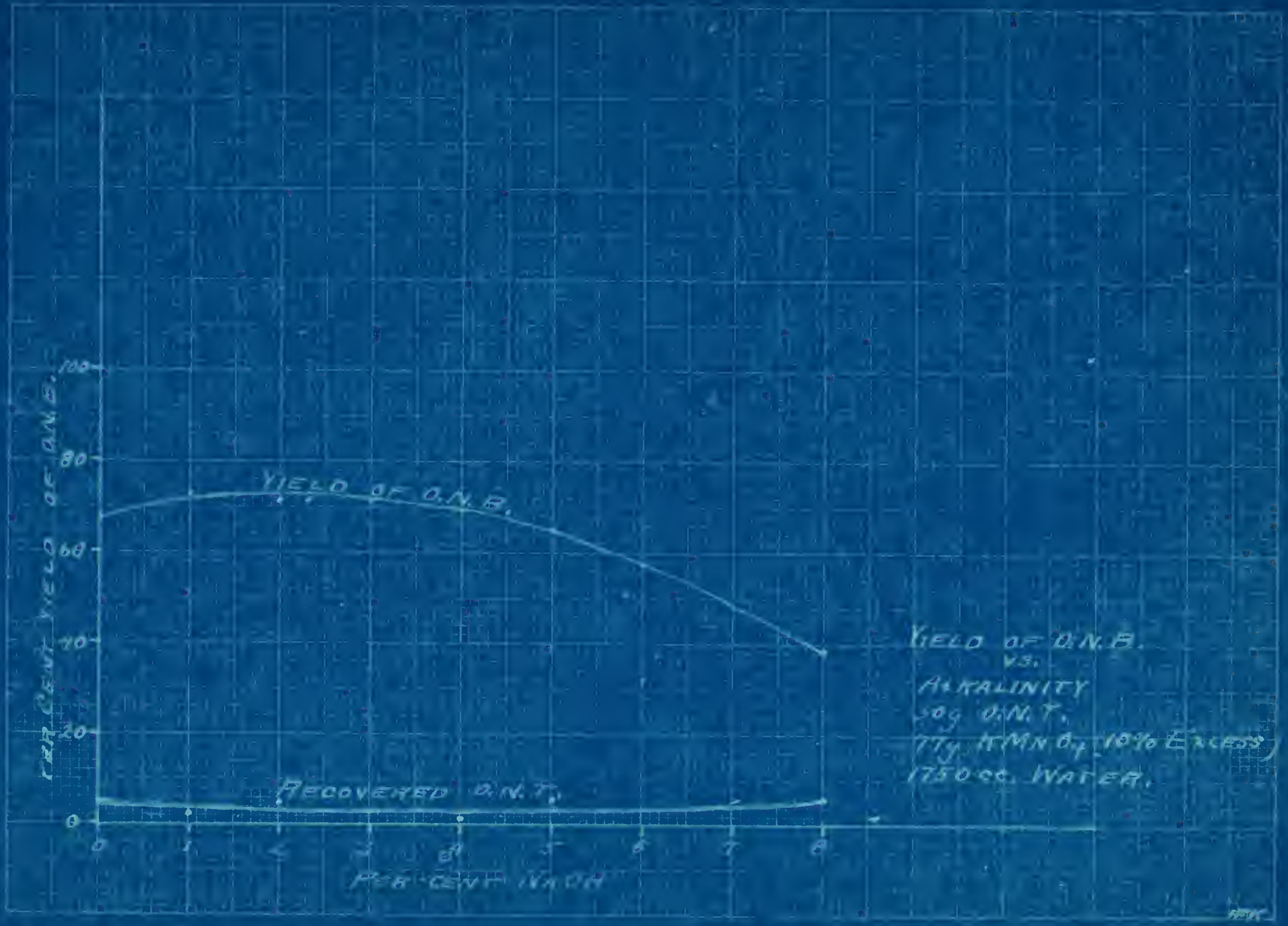
YIELD OF O.N.B.
RECOVERED O.N.T.
YIELD OF O.N.B.
VS.
ALKALINITY
50g. O.N.T.
77g. KMnO4 (10% EXCESS)
1750 cc. WATER.
PER CENT YIELD OF O.N.B.
0
20
40
60
80
100
0
1
2
3
4
5
6
7
8
PER CENT NaOH

FIG. J

ance of the product, however, becomes increasingly poor as the alkalinity is increased and, whereas with no caustic a snow white crystalline body is produced, with 6 and 8% caustic it becomes yellowish or even brown and of poor crystalline formation.

From the point of view of time required, and acid and alkali consumed it seems most desirable to operate at an alkalinity of 1%.

Per cent Yield of o-Nitro Benzoic Acid Vs. Alkalinity. 30 g. of O.N.T., 77 g. of $KMnO_4$, and 1750 cc. of Water.

Per cent NaOH	O.N.T. Recovered, g.	Per cent	Yield of O.N.B., g.	Per cent
0.00	1.35	4.50	24.80	67.80
1.00	.75	2.50	26.55	72.50
2.00	1.31	4.37	26.10	71.30
3.00	.85	2.84	26.00	71.00
4.00	.375	1.25	25.23	69.00
5.00	1.65	5.50	23.80	65.00
6.00	--		20.95	57.26
8.00	1.80	6.00	14.03	38.35

EFFECT OF PERMANGANATE

Taking the conditions of alkalinity and dilution previously determined, viz. 1% NaOH and 1750 cc. water, the quantity of permang-

anate used was varied from theoretical to 20% excess and the per cent excess plotted against yield of o-nitro benzoic acid (Fig.K). The effect of this variation was more pronounced than either of the previous variables and the curve shows a very pronounced maximum at 10% excess. The recovery of unchanged o-nitro toluene was not much affected by changing the amount of permanganate used, the variation in yield being due entirely to over or under oxidation of the same amount of o-nitro toluene.

The practice of adding the solid permanganate in four to six portions as was done throughout this work is not the best procedure and it is suggested that, for future work, some method of adding the permanganate continuously and so maintaining a low, uniform concentration be adopted. The reason for this will be seen from the sudden evolution of gas that occurs when permanganate is added to the hot solution. This gas is undoubtedly CO_2 and it shows the extreme over-oxidation

and resultant lowering of yields that this practice produces. One method that was tried was to hang a basket containing the permanganate under the reflux condenser so that the hot condensate would drip on it and carry through enough permanganate to maintain the proper concentration in the oxidizing solution. The amount added in this way can be controlled by the size of the permanganate particles and by the rate of boiling of the solution. The method, however, had one big objection. The o-nitro toluol distills withthe steam and, on running back with the condensate, much of it remains in the basket in direct contact with solid permanganate. This not only results in burning this part of the material, but also in coating the permanganate with oxides of manganese which hinder or prevent its proper solution. The net result of runs made in this way was a yield that averaged a few per cent lower than that obtained with the usual method. It would seem from this that in spite of its obvious defects, the method is not much worse than that of add-

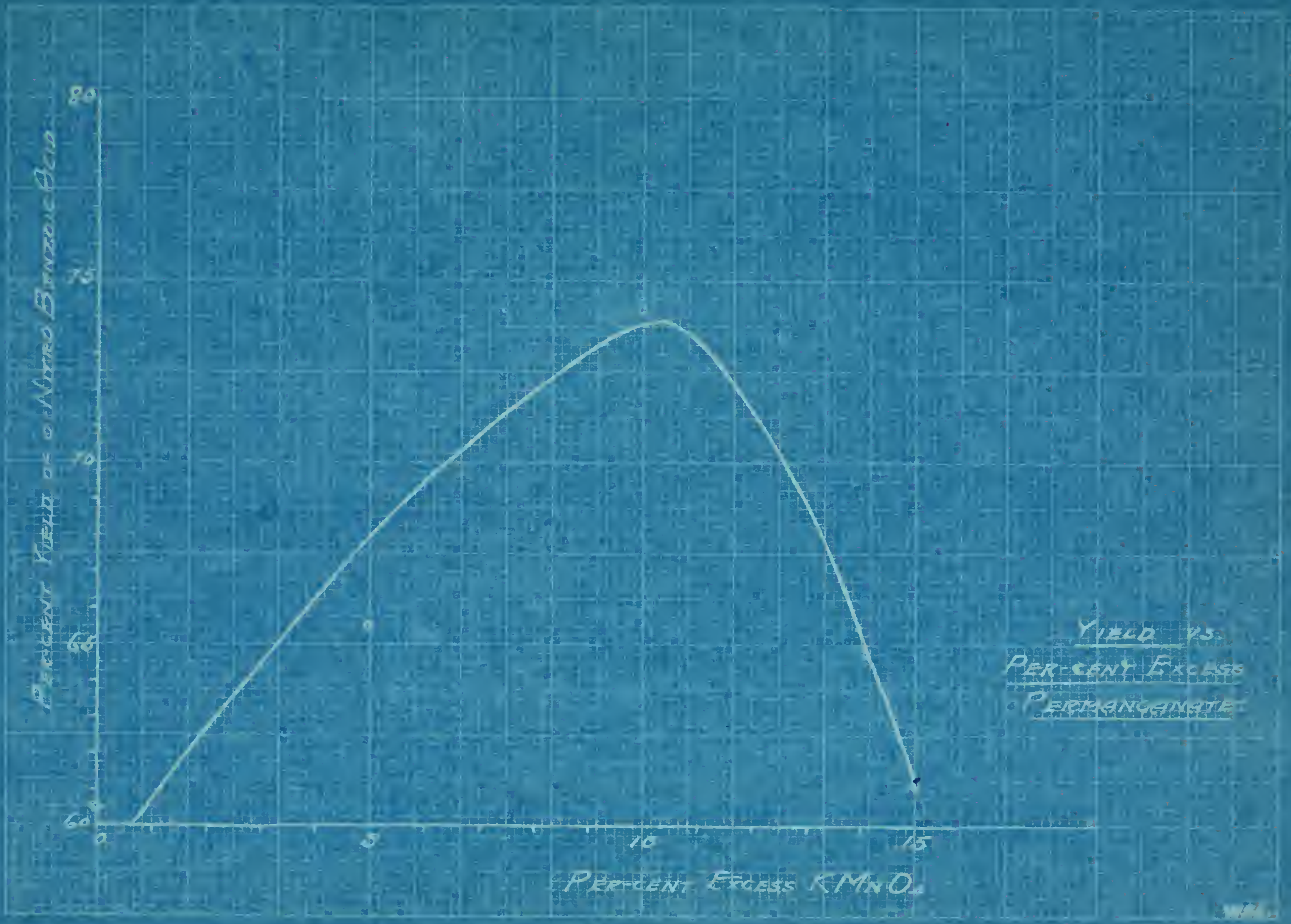
80
75
70
65
60
Percent Yield of o-Nitro Benzoic Acid
0
5
10
15
Per-cent Excess KMnO4
Yield vs.
Per-cent Excess
Permanganate

FIG. K.

ing the permanganate in successive portions, and it is probable that if a way were developed for feeding the permanganate into the reaction kettle continuously either dry or as a slurry and preferably below the surface of the liquid, a considerable increase in yield would result.

Per-cent yield of o-nitro benzoic acid
vs. Potassium Permanganate

30 g. O.N.T., 1750 cc. of Water and 1% NaOH

$KMnO_4$,g.	Per cent Excess	O.N.T. Rec'v'd.g.	Per Cent	Yield of O.N.B.	Per Cent
69.60	.00	2.86	9.55	22.07	60.40
73.10	5.00	2.22	7.40	23.90	65.40
77.00	10.00	1.20	4.00	27.15	74.20
80.04	15.00	2.75	9.16	22.34	61.10

THE SEMI-COMMERCIAL RUN

After having determined the best conditions for the oxidation of o-nitro toluene to o-nitro benzoic acid in alkaline solution, the following run was made.

The following conditions were maintained:

1. An alkalinity of 1% NaOH
2. A dilution of 30 g. of o-nitro toluene to 1750 cc. of water
3. A 10% excess of potassium permanganate

One and one-quarter pounds of commercial sodium hydroxide were dissolved in 125 pounds of water. This solution was heated nearly to boiling in a steam heated, enamel lined, reaction kettle fitted with a glass condenser. Two and one-eighth pounds of o-nitro toluene with one-eighth of the required amount of solid $KMnO_4$ were now added. This charge was boiled as fast as the glass condenser would allow until the $KMnO_4$ was entirely reduced. This took about one half an hour. The solid $KMnO_4$ was added in one-eighth portions every one-half hour over a period of four hours. After four hours of slow boiling, the reaction was thought to be complete because the solution showed no color of permanganate. Later, in drawing off the solution, quite a lot of $KMnO_4$ was found to have

settled out of the solution due to insufficient agitation.

The charge was now steam distilled to remove the unoxidized o-nitro toluene. This was done by heating the charge with steam and reversing the condenser, so that the distillate would not drop back into the reaction kettle. When the distillate came over water white the distillation was stopped as all the o-nitro toluene had been removed. The o-nitro toluene was extracted in the usual way and the per cent of recovery calculated.

The charge was now drawn from the reaction kettle and filtered through canvas in a large earthenware suction filter. The manganese dioxide was thoroughly washed with water and the filtrate was boiled for about one-half an hour in enameled containers. The filtrate was refiltered, after boiling, through a thick layer of sand in the same suction filter. The presence of $KMnO_4$ in the charge from the reaction kettle could be detected by

its action on the canvas filtering medium.

When the filtrate came through clear after the second filtration it was evaporated to the required volume in copper lined, steam heated kettles. It was thought that the filtrate could be reduced in volume in copper containers but this was found to be in error later on, as copper was found in the filtrate from the mother liquor.

This hot solution was now acidified with concentrated hydrochloric acid in an enamelled bucket. The solution was cooled to room temperature and the crystalline o-nitro benzoic acid was filtered off. The crystals were put in a centrifuge where the mother liquor was removed. They were further dried to constant weight in a steam drying oven. After adding the amount of o-nitro benzoic acid left in solution to our yield, the per-cent yield was calculated.

DATA

The Charge:-

125 pounds of water
1.25 " " sodium hydroxide

2.13 pounds of o-nitro toluene
5.44 " " potassium permangante

o-Nitro Toluene Recovered, lbs.	Per cent Recovery	Yield of O.N.B. lbs.	Per cent Yield
0.224	10.55	1.39	53.85

The low yield of o-nitro benzoic acid is doubtless due to the following reasons:

1. The fact that all the permanganate added was not used, due to insufficient agitation. This also accounts for the high percentage recovery of o-nitro toluene.
2. The loss of o-nitro toluene by the oxidation to carbon dioxide and water due to the addition of permanganate in large amounts.[1]
3. The loss of oxygen from the potassium permanganate.
4. The formation of a copper salt of O.N.B. with the copper of the kettles.

Copper kettles should not be used in reducing the volume of the solution, because the solution reacts with copper. This was shown to

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[1] After each addition of solid $KMnO_4$ to the charge, the evolution of a great amount of gas was noted. This was doubtless CO_2 from the O.N.T. and O_2 from the $KMnO_4$.

be true by getting a decided test for copper in the mother liquor. The fact that only about one-half of the calculated amount of HCl was added to acidify the solution shows that the alkali may have reacted with the copper. The low yield of o-nitro benzoic acid may be due to the formation of a soluble copper salt of the acid.

Enamelled containers were found to be the best for use in making this particular organic acid.

THE MANUFACTURE OF o-NITRO BENZOIC ACID

Of the various oxidizing agents used in oxidizing o-nitro toluene, potassium permanganate was found to be the best. The best conditions of alkalinity, dilution and excess of potassium permanganate were found to be the following:

1. An alkalinity of 1% NaOH
2. A dilution of 30 g. of o-nitro toluene to 1750 cc. water
3. A 10% excess of potassium permanganate.

The manufacturing process follows:- The required amount of caustic soda solution is placed in an enamel lined, steam heated suction kettle fitted with a reflux condenser. The solution is heated nearly to boiling when the o-nitro toluene is put into the hot solution with about one-eighth of the required amount of solid potassium permanganate. The solution is boiled until the $KMnO_4$ is decolorized when another portion is added. It will take about four hours for the entire amount of $KMnO_4$ to be reduced by the o-nitro toluene. The successive additions of one-eighth of the required amount of $KMnO_4$ every one-half hour was found to be satisfactory.

The unoxidized o-nitro toluene is now removed by steam distillation. This is done in the same kettle by using an ordinary condenser instead of a reflux condenser. It is advantageous to have the reaction kettle fitted with two condensers, a reflux and an ordinary condenser. By the turning of a valve one can be cut out. The o-nitro toluene can be removed by passing live

steam into the hot solution or by simply heating with steam. The latter method seems to be the better one in this instance because the volume of the solution is reduced, while in the former method the volume of solution is increased due to the water from condensed steam. The latter method was found to work satisfactory. When the distillate comes over water white all the o-nitro toluene is removed. This operation should take from one-half to one hour.

The hot charge from the reaction kettle is now sent to a filter press where the manganese dioxide is removed and thoroughly washed. The filtrate from the filter press is reduced to the required volume in a steam heated, enamel lined kettle. If any more manganese dioxide separates from the solution, the solution must be refiltered. If not, the solution is pumped to an enamel lined acidifying tank where concentrated hydrochloric acid is added to the hot solution until it is acid. The hot solution is allowed to cool to room temperature in the acidifying tank. Crystals

of o-nitro benzoic acid separate on cooling. The mother liquor is now drawn off from the crystals and the wet crystals go to the centrifuge where most of the solution is thrown out.

From the centrifuge, the crystals are sent to a steam drying oven where they are dried. The crystals are not further purified.

Starting with a good grade of o-nitro toluene, the o-nitro benzoic acid formed in the manner described is very pure. The product formed was crystalline, white and melted at 147.4° C.

The unoxidized o-nitro toluene must be removed to get a pure o-nitro benzoic acid. If there is enough o-nitro toluene unoxidized to warrant recovery, this can be accomplished as follows:-

The o-nitro toluene is removed from the water by extraction with ether. The water is removed from the ether solution of o-nitro toluene by withdrawing the lower layer.

The ether solution is dried over calcium chloride. Ther ether is now boiled off leaving the o-nitro toluene behind. The ether vapor is condensed and is used again.

The experimental results indicate that it will not pay to recover the unoxidized o-nitro toluene as an average of only 2.5% is unoxidized. Also the comparative cheapness of the material would not warrant recovery in such small amounts.

PROBABLE COST OF PLANT MAKING 50 POUNDS OF o-NITRO BENZOIC ACID PER DAY

In the following calculations, the yield is assumed to be 75% of theoretical.

Cost of Chemicals per Day

o-Nitro Toluene	54.5 lbs. at .25	$13.60
Potassium Permanganate	139 lbs. at .75	104.20
Hydrochloric acid (33%)	202 lbs. at .05	10.10
Sodium Hydroxide	31.6 lbs. at .05	1.58
		$129.48

COST OF EQUIPMENT

Building and Grounds (500 sq. ft. of floor space)	$2500
Two enamel lined reaction kettles (500 gals. capacity) at $750	1500
Two steel reflux condensers at $100	200
Two steel condensers at $75	150
One filter press at $200	200
One Steam heated, enamel lined Kettle (500 gals. capacity) at $500	500
One enamel lined acidifying and crystallizing tank, 250 gals. capacity at $200	200
One Centrifuge at $125	125
One Steam drying oven at $200	200
Two Pumps at $50	100
One 25 h.p. boiler and setting	1000
Piping and fittings	500
Total Investment..................................	$7170

Cost per Year:

Interest at 5%	358.50
Depreciation (5%)	358.50
Insurance and Taxes (1%)	71.70
	$788.70

OPERATING EXPENSES

Cost of Chemicals (300 days)	$38,844
Cost of Coal	1,080
Labor and Management	6,500
Maintenance and repairs	500
	$46,924.00
	788.70
	$47,712.70

50 X 300 = 15,000 lbs. of o-Nitro Benzoic Acid per year. $\frac{\$47,712.70}{15,000} = \$3.18.$

It is evident from the foregoing figures that it would be impossible to manufacture o-nitro benzoic acid by this method and make a profit at prevailing market quotations. The high cost of manufacture is almost entirely due to the cost of potassium permanganate. To show how the cost of manufacture could be lowered by using sodium permanganate made at the same plant, the following figures are submitted:

Cost of Sodium Permanganate per Lb.	$0.20
125 lbs/ at $0.20	25.00
Other Chemicals	25.30
	$50.30

300 X $50.30 = $15,090 (cost per year).

On this basis, o-nitro benzoic acid could be made for about $1.40 per pound.

The sodium permanganate could be made by the reaction of sodium hydroxide and manganese chloride. The sodium manganate formed could be oxidized to sodium permanganate by chlorine or electrolytic oxygen. As sodium permanganate will not crystallize from the solution in which it is formed, this solution could be used as the oxidizing solution.

SUMMARY

O-nitro toluene can be oxidized to o-nitro benzoic acid by alkaline permanganate with yields as high as 80% and 2% of unchanged o-nitro toluene recovered.

The results of this study may be briefly summarized as follows:

1. Of the oxidizing agents, chromic acid, alkaline ferricyanide, nitric acid, and permanganate, the latter was found most suitable.
2. The best concentration was one part by weight of o-nitro toluol to sixty parts of water.
3. The most advantageous alkalinity was a one per cent solution of 90% commercial sodium hydroxide.
4. Best results were obtained when 10% excess potassium permanganate over theoretical was used.
5. Best operating conditions are as outlined above with the following qualifications:
    a. Continuous and uniform addition of permanganate.
    b. Vigorous boiling or other agitation at 100°.
    c. Use of enamelled vessels.

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